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QUARTERLY PROGRESS REPORT

Office of Naval Research

N7on: -292 T.O.5

March 15, 1953

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Department of Physics

University of Missouri

Columbia

Submitted by:

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INTRODUCTION

This report covers research activities carried out under Contract N7onr-292 T.O. 5 during the quarter ending March 15, 1953.

Ten problems are currently active under this research program and of these, five are related to the electronic properties of magnesium oxide. Our considerable interest in this material stems from the availability of high purity, single crystals grown in the electric arc furnace. The very high resistivity of this insulator type material makes it characteristic of other materials in this class and gives it many interesting properties not found in the other divalent alkaline earth oxides previously studied in this laboratory. Samples of these "home grown" crystals have been distributed to other laboratories for studies of secondary emission and optical absorption.

A paper by Virgil L. Stout appeared in the January 1, 1953 issue of the Physical Review entitled, "Luminescence and Thermionic Emission of Barium Oxide". It represents a condensation of our Technical Report No. 12.

PERSONNEL

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seven-twelfths time

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Machinist

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Secretary

Eileen Levine

full time

* * * * *

Professor L. V. Holroyd is assisting the program by directing the studies requiring the use of radioactive isotopes. Services of the Glass Blowing Shop, the Science Instrument Shop, the Spectroscopic Laboratory and the X-ray Diffraction Laboratory were used in this research program.

1. Luminescence Studies - (Gandy)

Spectral and time decay measurements have been made recently on the cathodoluminescence of MgO. This MgO sample consists of crushed crystals which were grown here. The sample was settled in an alcohol suspension to obtain a particle size from 10 to 30 μ . The sample was applied to a pure nickel base by dropping the suspension from a glass rod and then allowing it to air dry. A normal tube processing was followed and the tube was sealed off the vacuum system at a pressure of less than 10^{-7} mm Hg.

Fig. 1 shows the cathodoluminescence spectra obtained for this sample using a bombarding potential of 1500 V-DC and a bombarding current density of about 50 $\mu\text{a}/\text{cm}^2$. Three luminescence bands were observed whose maxima are at photon energies of 3.7 ev, 2.6 ev, and 2.3 ev. Fig. 2 shows that the peak intensity of the 3.7 ev band increases from liquid air temperature, reaches a maximum at a sample temperature of about 350°K, and then decreases rapidly with increasing sample temperature. The same general behavior is observed for the 2.6 ev band except that this band seems to reach a maximum at a somewhat higher temperature (approx. 425-475°K). The 3.7 ev and 2.6 ev bands have equal peak intensities at a sample temperature of about 480°K. Above 500°K the 3.7 ev band intensity

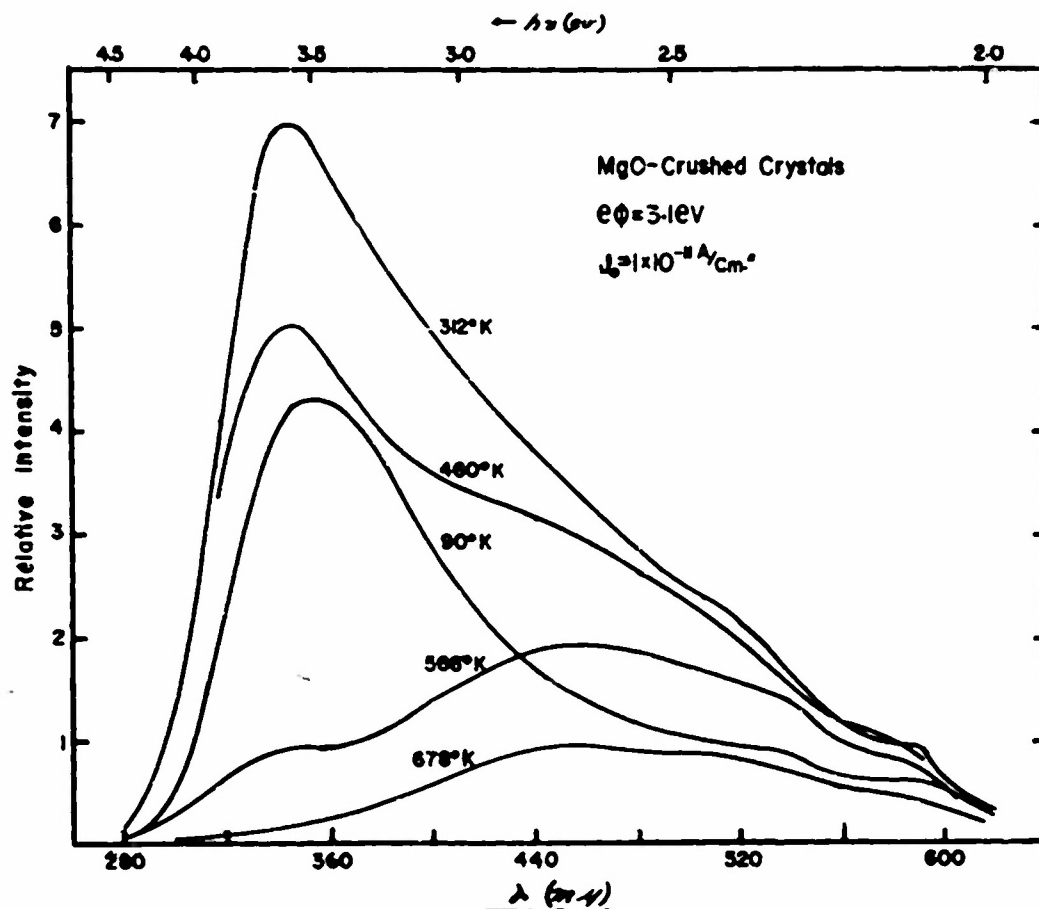


FIG. 1

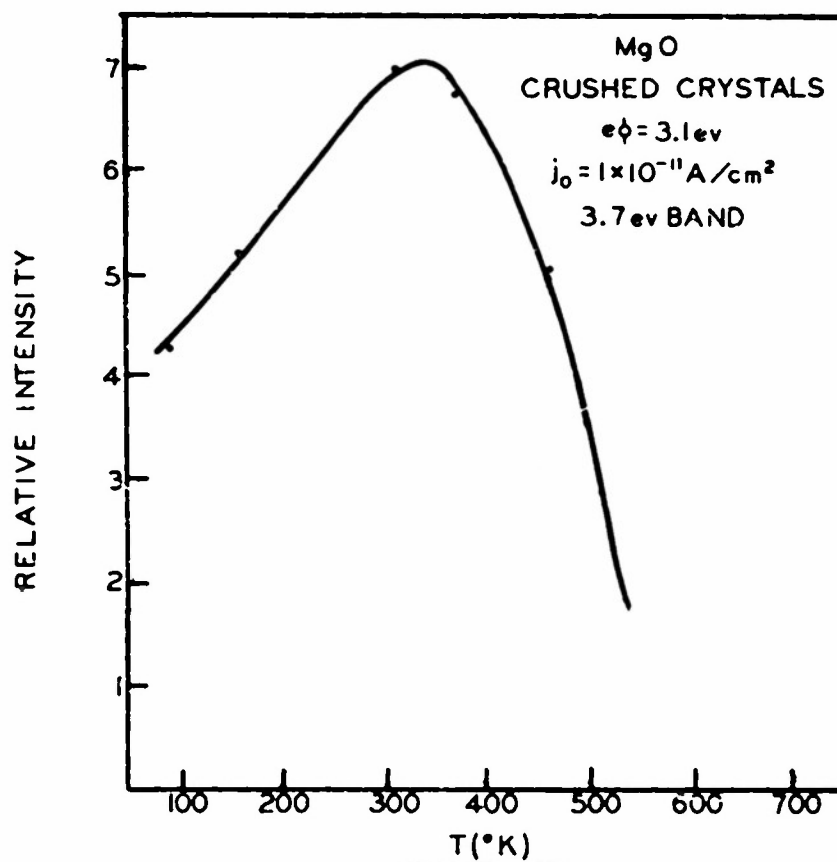


FIG. 2

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drops quite rapidly with increasing sample temperature, whereas the intensity of the 2.6 ev band decreases but not nearly as fast. This is shown in Fig. 1.

Auxiliary experiments were done to determine the dependence of the luminescence on bombarding current and voltage. The current densities were varied from $25 \mu\text{A}/\text{cm}^2$ to $400 \mu\text{A}/\text{cm}^2$ at a constant bombarding potential with the sample temperature maintained at liquid air temperature. The total luminescence output as well as the spectral distribution of luminescence was observed to be linearly related to the bombarding current density. The current was kept constant and the bombarding potential was varied from 250 VDC to 2000 VDC with sample again maintained at 90°K . Within experimental error the spectrum shape remained the same. However, the total luminescence output changed more rapidly than did the bombarding potential.

No spectrum or intensity changes were observed after bombarding the sample for lengths of time up to five hours.

A $4 \mu\text{s}$ pulse (current density approx. $100 \mu\text{A}/\text{cm}^2$) of electrons was allowed to bombard the sample and the luminescence of the 3.7 ev and 2.6 ev bands were separately monitored over a temperature range from 90°K to 650°K . The fall time of the electron gun grid pulse was measured

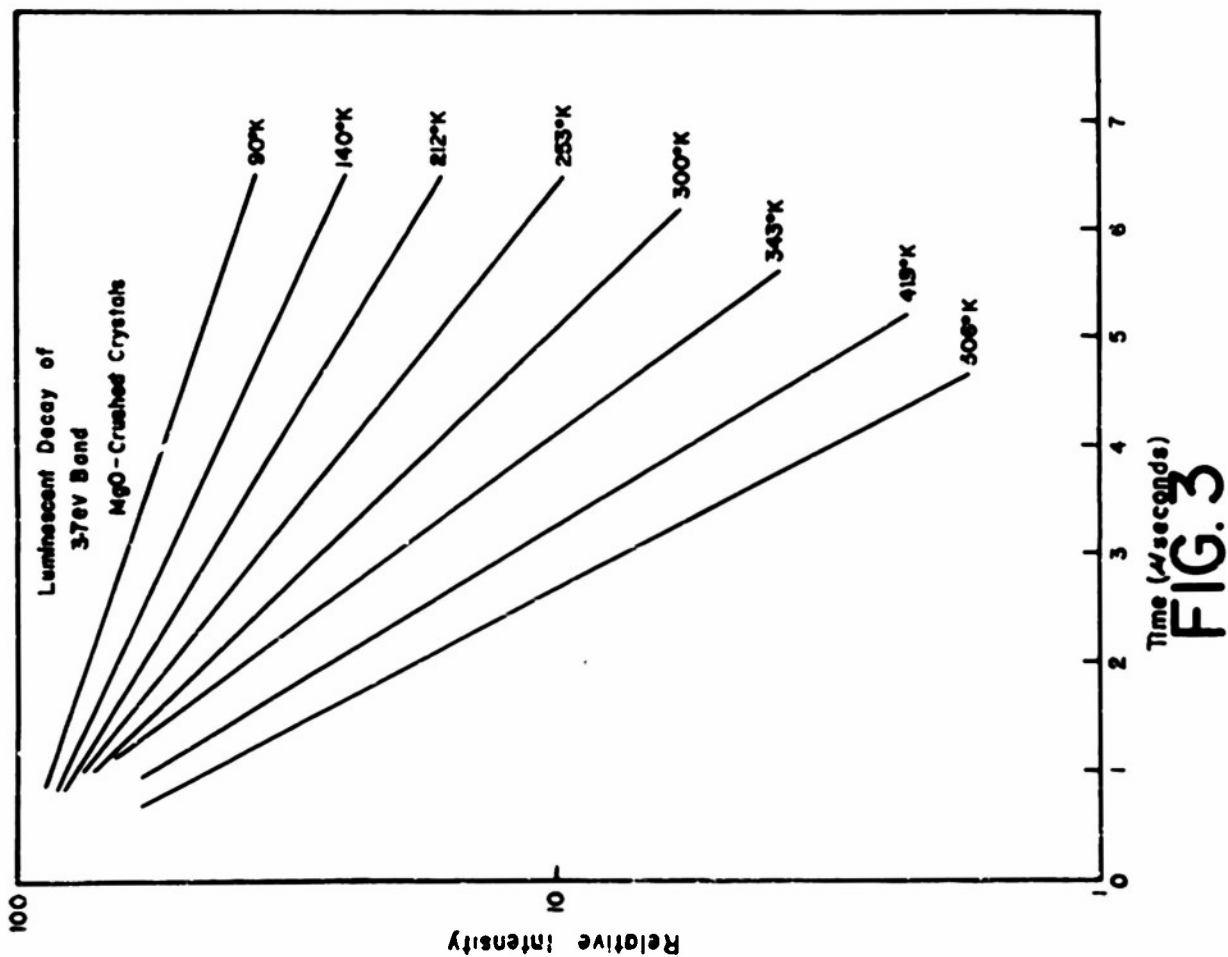


FIG. 3

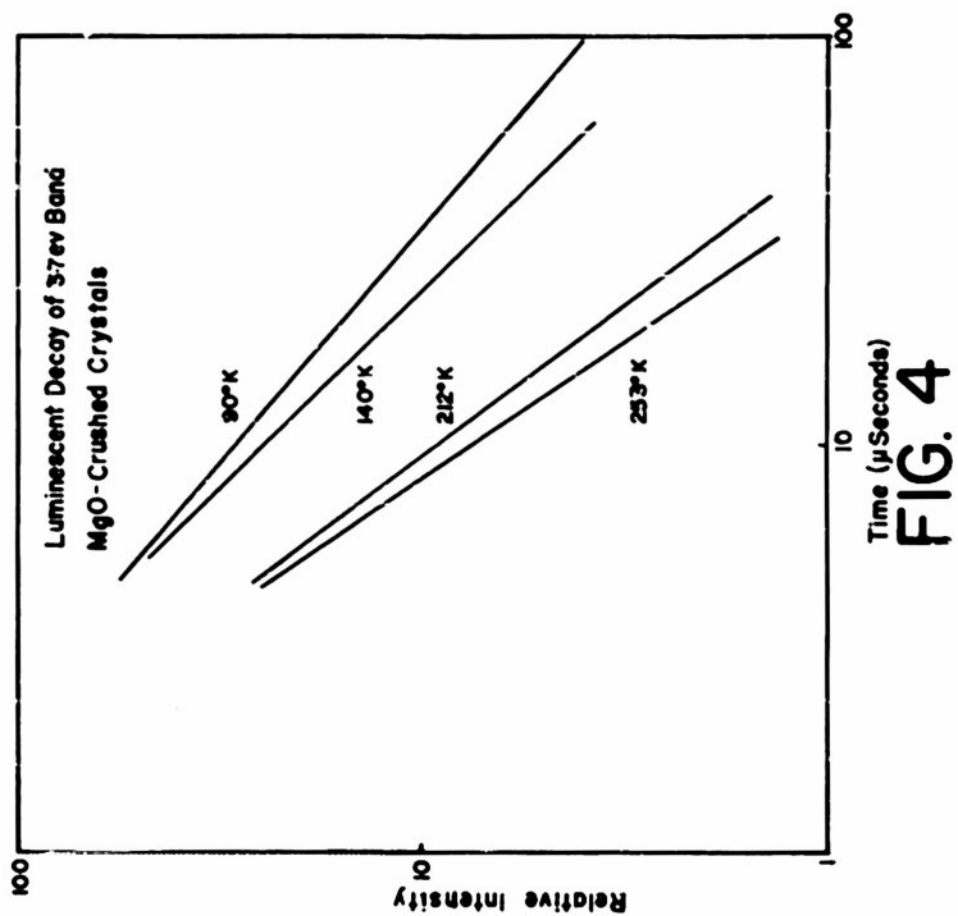


FIG. 4

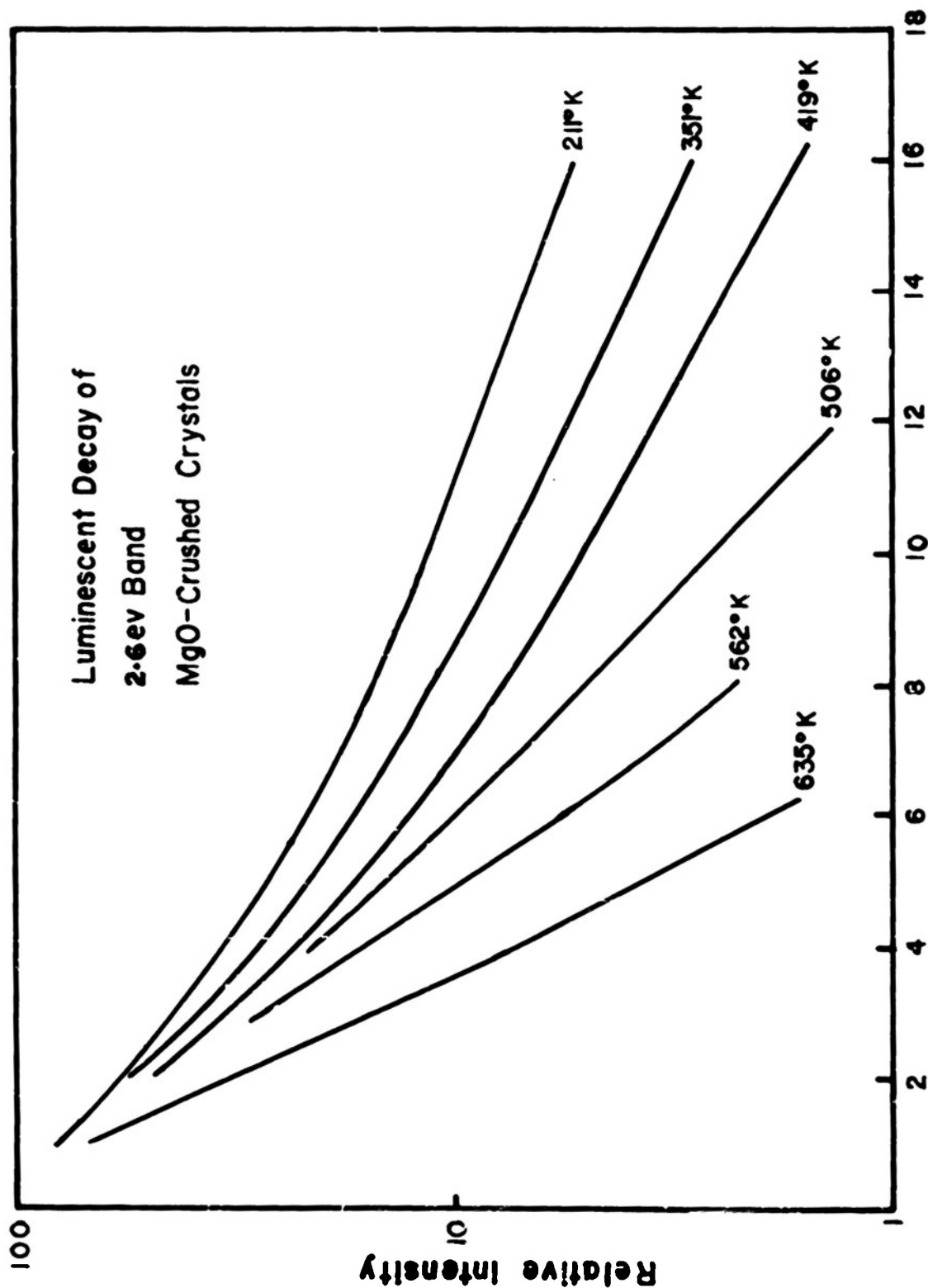


FIG. 5

to be about $1\ \mu\text{s}$, and that of the bombarding pulse was about $0.5\ \mu\text{s}$. The time decay of the $3.7\ \text{eV}$ band from $1\ \mu\text{s}$ to about $7\ \mu\text{s}$ after the pulse is exponential in the temperature range from 90°K to about 500°K . This is shown in Fig. 3. A study of the temperature dependence of this decay indicates that the electrons involved in this decay do not come from a single set of trapping levels. From about $8\ \mu\text{s}$ to $120\ \mu\text{s}$ the time decay of the band seems to be a power law for sample temperatures ranging from 90°K to about 250°K as shown in Fig. 4. The exponent varies from -0.9 at a sample temperature of 90°K to -1.5 at 253°K . The temperature dependence of this slope has not yet been determined.

Fig. 5 shows the time decay of the $2.6\ \text{eV}$ band for several sample temperatures. Although these curves do not indicate an exponential dependence, they give a much poorer fit to a straight line on a log intensity versus log time plot than does the $3.7\ \text{eV}$ luminescence, which indicates that the decay of this band is not a power law decay.

In order to determine the effect of bombarding current density on the decay of the $3.7\ \text{eV}$ band, the sample was maintained at 90°K and bombarded with $4\ \mu\text{s}$ pulses of electrons with current densities ranging from $40\ \mu\text{A}/\text{cm}^2$ to about $4000\ \mu\text{A}/\text{cm}^2$. The exponent in the power law decay did not change (within experimental error) with changing bombarding

current density; however, the short time exponential decay rate increased slightly with increasing bombarding current density.

The tube containing this sample was resealed onto the vacuum system using a gas crack-off tip and the sample was then held at 925°K for 15 minutes in a pressure of 10^{-2} mm of oxygen. Spectral measurements were then made on the sample as was done before. Analysis of these spectra showed no appreciable differences from those of the original sample.

Another tube was assembled and processed using a single crystal of MgO as the sample. The dimensions of the single crystal are $3 \times 5 \times 0.5$ mm. A platinum electrode was applied to the back side of the crystal. Preliminary spectral measurements on this sample indicate the presence of the three bands found with the crushed crystal sample, with the same spectrum shape. However, another band has been found in the $4.8 - 5.2$ eV region. The intensity of this band increases by about a factor of five upon reducing the sample base temperature from 304°K to 90°K . The total luminescence output of the crushed crystals sample is about 200 times as large as that of the single crystal sample when compared over commensurate spectral regions.

Data concerning the dependence of the growth and decay of luminescence on bombarding time for the crushed crystals sample have been obtained,

but not as yet reduced. It is planned to make more complete spectral and decay measurements on the single crystal sample soon.

2. Thermionic Emission at Low Temperatures - (Heath)

In the last Progress Report it was stated that measurements of the thermionic emission from the iron cathode using the electron counting technique were rather difficult to interpret. In the hope of clearing up this difficulty measurements of the thermionic current were made using a vibrating reed electrometer. With this method the current could be collected at the first dynode or, if the shielding doors were closed, at the grid itself. It was thus possible to determine what fraction of the total emission current actually reaches the first stage of the multiplier.

Measurements showed this to be about 50 - 60 %.

Several sets of data were taken with the vibrating reed electrometer using both the first dynode and the grid doors as the collector over the temperature range of 950 - 1200°K (Curie point is 1050°K). Richardson plots of this data gave a work function of about 3 ev. In addition, the current measured was roughly four orders of magnitude higher than what would be expected from Wahlin's data¹.

Counting measurements made over approximately the same temperature range do not yield such good results. The points scatter considerably and

1. H.B. Wahlin, Phys. Rev. 61, 509 (1942).

only a rough estimate of the slope of a Richardson plot is possible. The data indicates a work function in the neighborhood of 4 ev. Also, the magnitude of the emission current measured in this way is roughly equal to that expected on the basis of Wahlin's data¹. However, this is no encouragement as it is much more likely that the vibrating reed measurements are more accurate and dependable than counting measurements (see below).

Because of the great discrepancy between the experimentally observed data and that which has been published by Wahlin¹ and Krishnan and Jain², it seems very likely that the iron cathode is not pure iron. The iron may contain impurities as a result of its manufacture. A more probable explanation is that the surface of the iron is covered by some iron compound which does not decompose during the outgassing of the cathode. Perhaps the residual gases in the tube may also have an effect, but it is felt that this effect should be eliminated by heating the cathode at about 1100° K. This is partially borne out by the following experiment: The tube was allowed to stand idle for about two weeks. Without any preliminary heating, a series of current measurements at various temperatures was made with the vibrating reed electrometer. A Richardson plot showed that the work function above the temperature of about 1050° K was unchanged from

2. K.S. Krishnan and S. C. Jain, Nature 170, 759 (1952).

the value that had been obtained before the two week layoff (3.06 ev). Below this temperature, however, the work function was markedly different having a value of 2.20 ev. With subsequent heating this break in the Richardson line faded away until a smooth line resulted. It should be noted that the temperature at which the break occurs is the Curie temperature. Whether this is a significant fact or not is still to be determined.

Because of the many difficulties encountered with the iron cathode and because of the rather anomalous results obtained, it was decided to study the thermionic emission from a tungsten filament at low temperatures.

The thermionic constants of tungsten are accurately known ($\phi = 4.54$ ev, $A = 60 \text{ amp/cm}^2 \text{ } ^\circ\text{K}^2$) so that it was felt that this would serve as a check on the accuracy of our measuring technique.

The tube used is very similar to that used for the iron measurements except that the emitting surface is in the form of a tungsten wire filament. In the guard ring structure surrounding the filament, there is a door which may be opened to expose the central portion of the filament so that the emitted electrons are able to travel directly to the first stage of the multiplier through a wire grid. The temperature of the filament is obtained by measuring the voltage drop along the filament and the filament current and then applying the end loss corrections accord-

ing to Jones and Langmuir³.

Measurements of the emission current made with the vibrating reed electrometer give a work function of 4.48 ev and an A constant of 72 amp/cm²°K² which are in good agreement with the accepted values. This then gives us a standard against which we can compare the electron counting results.

Thus far only preliminary measurements using the electron counting technique have been made with the tungsten filament. These indicate that the current measured by electron counting is approximately 1/1000 of that measured with the vibrating reed.

Further work is planned with the electron counting technique and the tungsten filament tube to see if there is any explanation for the poor results obtained with the electron multiplier.

3. Ba₂SiO₄ Interface Thickness Versus Life - (Affleck, Holroyd)

A series of six cathodes made on "225" Ni buttons about .020" thick and containing .22% silicon impurity, have been prepared with BaCO₃ containing Ba¹⁴⁰. However, the oxide coating on several of these cathodes cracked and lifted from the base metal during the conversion process.

3. H.A. Jones and I. Langmuir, General Electric Review 30, 310 (1927).

The remaining cathodes appeared satisfactory and were put on life test.

After about 50 hours they, too, cracked and lifted.

It appears that the coating material is wet when deposited on the cathode base. In order to overcome this difficulty which is caused by space limitations in the spray box an extension has been attached to the box to increase the distance between the spray gun and cathode.

Another series of cathodes is now in preparation for interface thickness measurements.

4. Electrical Conductivity and Thermoelectric Power of MgO - (John)

Measurements of the conductivity of single crystal MgO (our melt of April 23, 1952) have been made between temperatures of 1510° K and 1125° K. The value of the specific conductivity was $2.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1510° K and $9 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 1125° K. The plot of $\log \sigma$ vs $1/T$ was fairly linear in this region. The slope of this curve gave an activation energy of about 3.0 ev. These results should be compared to those on the compressed MgO powder (density of compressed material $.5 \text{ g/cm}^3$; single crystal density 3.65 g/cm^3) which gave specific conductivities about 10 times smaller at the upper temperature and an activation energy of 3.2 ev⁴.

Thermoelectric power measurements on the same crystal were made

4. Quarterly Progress Report, December 15, 1952.

at several temperatures between 1400°K and 1220°K . The warmer electrode was always positive in agreement with the compressed powder result. The values of dE/dT ranged from 2.5 to $3.0\text{ mv}/^{\circ}\text{K}$. The data are not sufficiently good to determine the variation of dE/dT with temperature.

The tube has been reconstructed recently. The thermocouples have been relocated with the cold junctions further away from the heated cathodes in the hope that this change will contribute to more consistent thermoelectric power data. Work will be continued on single crystal MgO .

5. Electron Emission from MgO - (Stevenson)

Two new photoelectric studies have been made since the last report. A quantitative analysis of the photoelectric yield is not presented in this report because of the uncertainty in monitoring the light intensity in the spectral region beyond the threshold. The extrapolated intercept of a plot of photoelectric emission yield vs. $h\nu$ for a cathode surface of pulverized crystals of MgO gives a photoelectric threshold of 3.4 eV. No thermionic emission measurements could be made on this tube because of a defective filament. However, in Sect. 1 of this report Mr. Gandy reports a thermionic work function of 3.1 eV on a similar sample. This value is consistent with values previously reported⁵.

5. Quarterly Progress Report, September 15, 1952

A Norton single crystal of MgO was mounted between two tantalum cups as described in the last progress report⁴. The photoelectric yield was studied as a function of photon energy. A photoelectric threshold of approximately 3.5 ev was obtained. The spectral distribution is uncertain because of charging of the crystal. This charging effect may be calculated quite readily if it is assumed that photoconductivity is the principal mechanism in the transport of charge through the bulk of the crystal. The calculation indicated that photoconductivity is the limiting factor for photoelectric emission at room temperature. Photoelectric emission from single crystals at elevated temperatures will be studied with the hope of eliminating this charging effect. No consistent results have been obtained at this time on the thermionic activity of the sample. The following table compares the data taken on three different types of MgO cathodes.

Surface	Thermionic Work Function	Photo-electric Threshold	Quantum Efficiency at 330 mμ	Calculated "Electron Affinity"
Sprayed MgO powder (Baker).	3.0 ev	3.4 ev	3×10^{-8} e/quantum	2.6 ev
Pulverized MgO single crystals (M. U)	3.1 ev ⁶	3.4 ev	5×10^{-7} e/quantum	2.8 ev
Single crystal of MgO (Norton)	-----	3.5 ev	1×10^{-8} e/quantum	-----

6. Gandy, This report, Section 1.

The electron affinity was calculated using the assumption that the Fermi level was halfway between the bottom of the conduction band and the photoelectric threshold. There are some reasons why this assumption may not be valid. The Fermi level may undergo large changes with temperature. The photoelectric emission may be a two step process. Then the threshold might not be for transitions from the crystal to the vacuum but for transitions between levels. It is hoped that an experiment suggested by Mr. Goodman and which is a variation of one described in Mott and Gurney⁷ may yield a better value of the electron affinity.

One important change in instrumentation has been incorporated into the experimental apparatus. The use of distilled water for cooling has greatly increased the lifetime of the AH-6 high pressure mercury arc in addition to eliminating a deposit formation from tap water. The system has been modified to use a 15 gallon reservoir of distilled water which is pumped at a rate of 15 liters per minute. The reservoir is large enough to allow the lamp to be operated for two hours before the temperature of the water rises too much. In addition, the housing for the mercury arc has been tinned to reduce the metallic ion concentration.

7. Mott and Gurney, Electronic Processes in Ionic Crystals (Oxford 1948) p. 73.

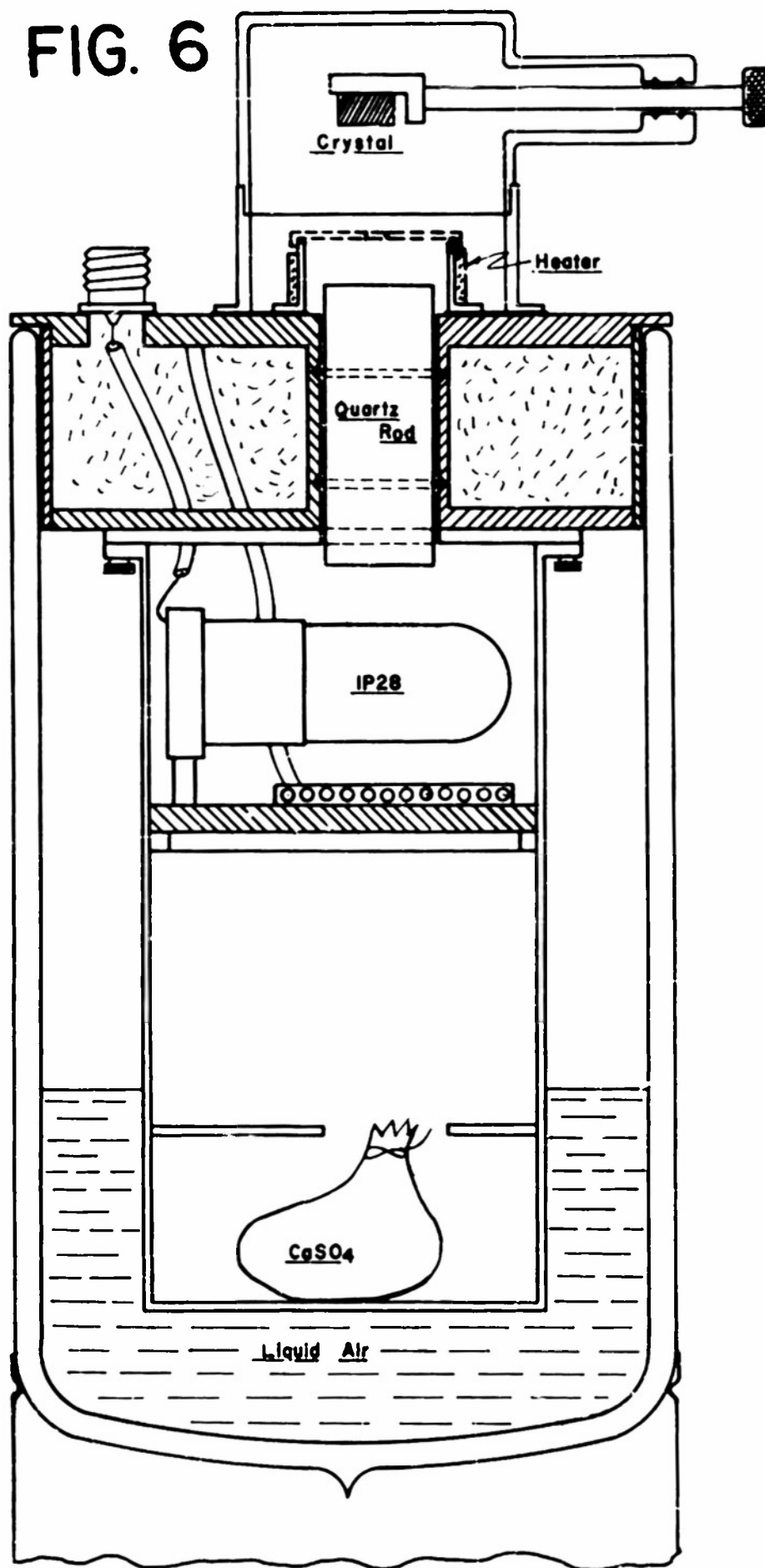
6. Luminescence of MgO - (Eisenstein)

Several improvements have been made in the photon counting techniques used for studying the x-ray excited luminescence of MgO. By more effective light shielding of the photomultiplier assembly the background counting rate has been reduced to less than one count per second. A solid fused quartz rod, three inches long, has been inserted between the source and the photomultiplier to increase the optical coupling. This addition has given a sensitivity increase of a factor of twenty. Thermal conductivity of the quartz caused icing and fogging of the upper face which was eliminated by using an electrical heater. These details of the construction of the multiplier assembly are shown in Fig. 6.

In order to extend the range of sensitivity of the instrument to permit the measurement of intensities above 10^5 counts per second, a set of apertures were made and calibrated. These are placed over the upper end of the quartz rod on the heater assembly, see Fig. 6. By means of these apertures the range of practical measurements is from 1 to 10^8 photons per second.

Since it is desirable to make measurements on a given sample over long periods of time (up to several weeks), a set of standard light sources were prepared. By means of these the instrument may be calibrated periodically.

FIG. 6



A long lifetime radioactive source mixed with a phosphor powder was mounted in a block of plastic. Four such sources produce counting rates of 135, 2800, 7900 and 50,000 counts per second. The photon counter shows day to day variations in sensitivity of less than 5%.

Studies of the x-ray excited luminescence of MgO may be summarized by the following experiments:

1. The December 15, 1952, Progress Report described results obtained on Norton, single crystal samples from which the luminescence decay could be detected for several days. These crystals appeared magenta under x-ray irradiation due to a blue luminescence band plus a high intensity in the red region. Subsequent studies of home grown MgO crystals reveal only the blue band and the luminescence decay is such that it has been measured over six weeks after it was exposed to x-rays for a period of sixty seconds. From 10^2 to 10^6 seconds the luminescence decay followed the law $I = kt^{-n}$ with n from 0.6 to 0.7. At 3×10^6 seconds the counting rate was still above 10^3 counts per second. It is apparent that the fit of experimental data to the time dependence shown above can only be an approximation. Unless n becomes greater than unity the total luminescence energy integrated over all time will not be finite.

2. A sample holder consisting of a copper block attached to the bottom

of a metal cup has been constructed to mount on top of the photon counter. Liquids placed in the cup permit the temperature of the sample to be changed rapidly or to be held constant. Fig. 7 shows a series of plots of the luminescence decay at several temperatures. In each case the sample was irradiated for 25 seconds, allowed to decay at room temperature for 420 seconds, and then the sample temperature was rapidly changed to the values shown. Increasing the temperature causes an increase in intensity and a more rapid rate of decay whereas lowering the temperature reduces both the intensity and its rate. The values of n , the slopes of the curves, are shown. After each run the crystal was completely bleached by placing it in an oven at 100°C for 15 minutes. At this temperature the crystal would glow visibly exhibiting typical glow curve characteristics.

3. All irradiations were made using a copper target x-ray tube operated at 37KV and 12 ma. The effect of increasing dose between 1 and 625 seconds is seen in Fig. 8. There is no apparent saturation within this time range although several hours of irradiation do not produce a very much greater intensity than that of the upper curve. It is of particular interest to note that the slopes of these curves change perceptibly with dosage. This is an important factor to consider in attempting to set up a mechanism for the process which is involved.

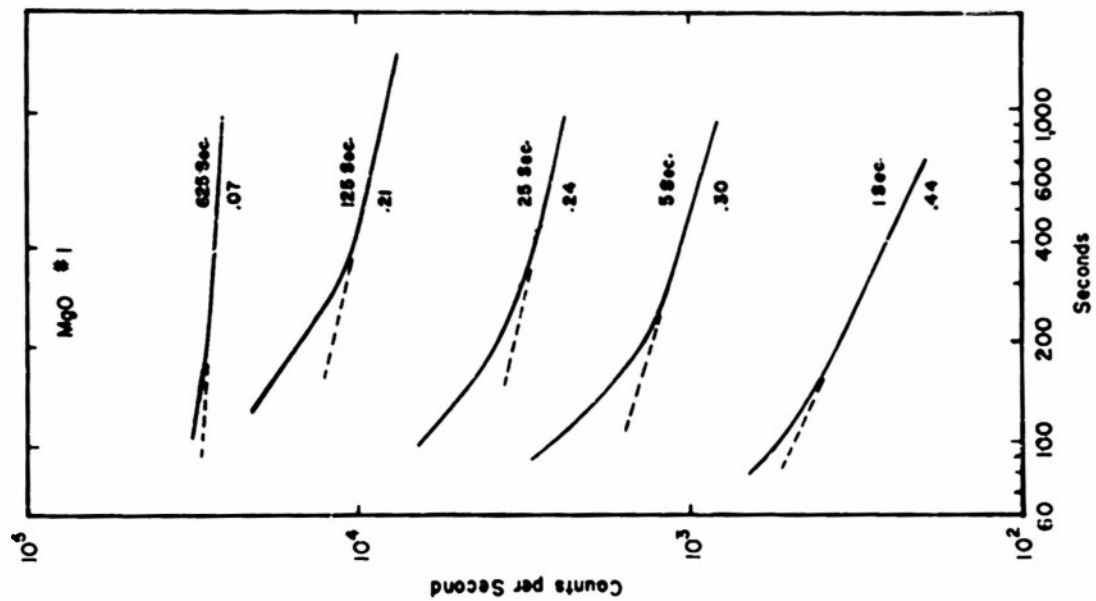


FIG. 8

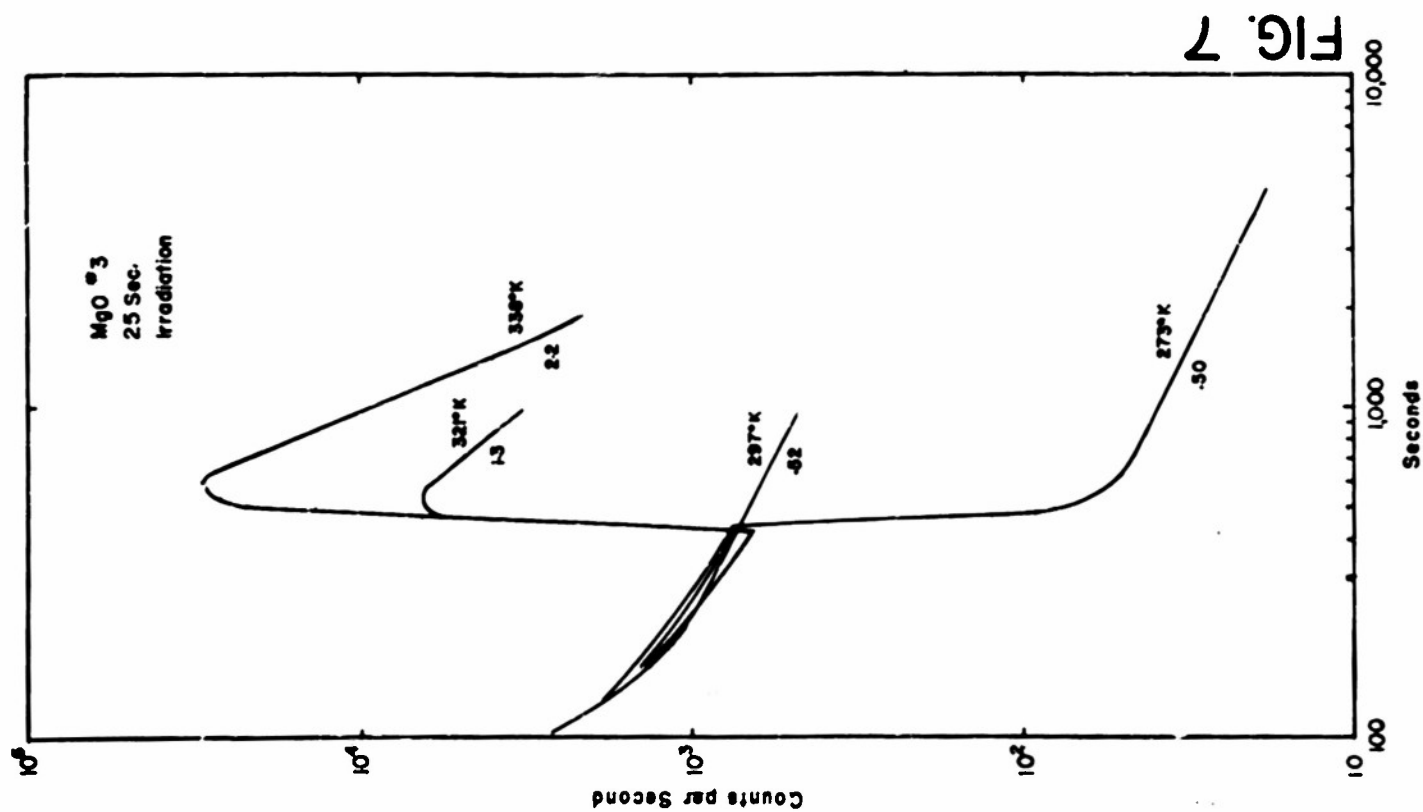


FIG. 7

A somewhat similar experiment was performed in which the total dose remained the same but the rate at which it was delivered was changed by a factor of six. Within experimental error the luminescence decay was the same in each case.

4. Toward the end of the quarter a Machlett AEG-50, tungsten target x-ray tube was set up for crystal irradiation work. X-rays were allowed to fall on a MgO crystal attached to the entrance slit of a Gaertner monochromator. The resulting luminescence radiation passed through the monochromator, was deflected by means of a front surface mirror and entered the photon counter. With the slits set for a band pass of 8 mμ at 400 mμ the counting rate had a maximum value of 10^4 counts per second. A scan of the luminescence spectrum revealed an ultraviolet band at 260 mμ in addition to the 360 mμ band which is responsible for the blue color. When corrected for monochromator dispersion and multiplier sensitivity these bands were of about equal intensity at room temperature. However, all intensity measurements reported earlier refer only to the 360 mμ band because of the spectral response characteristics of the 1P28 detector.

A sample of pulverized, home grown MgO crystals when similarly treated showed no luminescence at 260 mμ and the visible band was shifted to peak at 410 mμ. The explanation of this effect of pulverizing

on the ultraviolet band of the luminescence spectrum is not understood, however it may be noted that it was also found in the cathodoluminescence studies by Gandy, Section 1.

No attempt will be made to explain these various phenomena now, however theoretical studies along this line are in progress, see Section 10b. Similar, long time luminescence decay studies are being undertaken on NaCl and KCl by a student whose work is not supported by the ONR. As significant developments are made, they will be reported here for comparison with the MgO results.

7. Infrared Transmission of Thin Semiconductor Films - (Brouillette)

The absorption tube has been reconstructed and a preliminary survey of the lead sulfide cell region (.6 to 2.5 micron) has been started. The tube is essentially the same as that described by Stout in an earlier report⁸. A BaO film of approximately 5 micron thickness has been evaporated and the absorption recorded before activation. No marked features have been observed. The film does tend to be more transparent at the longer wavelengths. An attempt to activate the sample will next be made to see if any change takes place with activation.

Certain experimental difficulties have become apparent. A tube with

8. Quarterly Progress Report, December 15, 1950

certain new features will be constructed to circumvent them. These include:

- 1) An optical stop in proximity to the sample to mask it and suppress light passing around the edges;
- 2) An evaporation mask to prevent coating the metal sample holder which might contribute to thermionic emission;
- 3) Re-mounting the evaporator on a separate press with a barium evaporator so that free Ba may be evaporated onto the sample to influence activation.

When this survey is completed the spectrometer will be rearranged to cover wavelengths down to .25 microns in order to observe the absorption edge reported by Tyler⁹. A measurement of absorption in this region will check the film thickness as determined by evaporation temperatures.

8. Field Emission - (Spicer)

The phosphor coating in the field emission tube mentioned in the last Progress Report was damaged while opening the tube to replace the field emission point. The method of obtaining phosphor films has been greatly improved with the construction of a tank in which the film can be compressed by means of a slider while it is floating on water. The process is much quicker and easier than the one described previously.

After a uniform, tightly packed, mono-particle film has been floated, it is deposited on a Pyrex glass plate which is raised through it. Care must

9. W.W. Tyler, Phys. Rev. 76, 1887 (1949).

be taken to compress the film continuously as the plate is raised through the surface in order to keep it intact. A second field emission tube has been completed with a phosphor plate obtained in this way.

A report has been prepared which gives the details of the process of preparing the thin phosphor screens and also tungsten field emission points. Copies of this report will be sent to anyone requesting them.

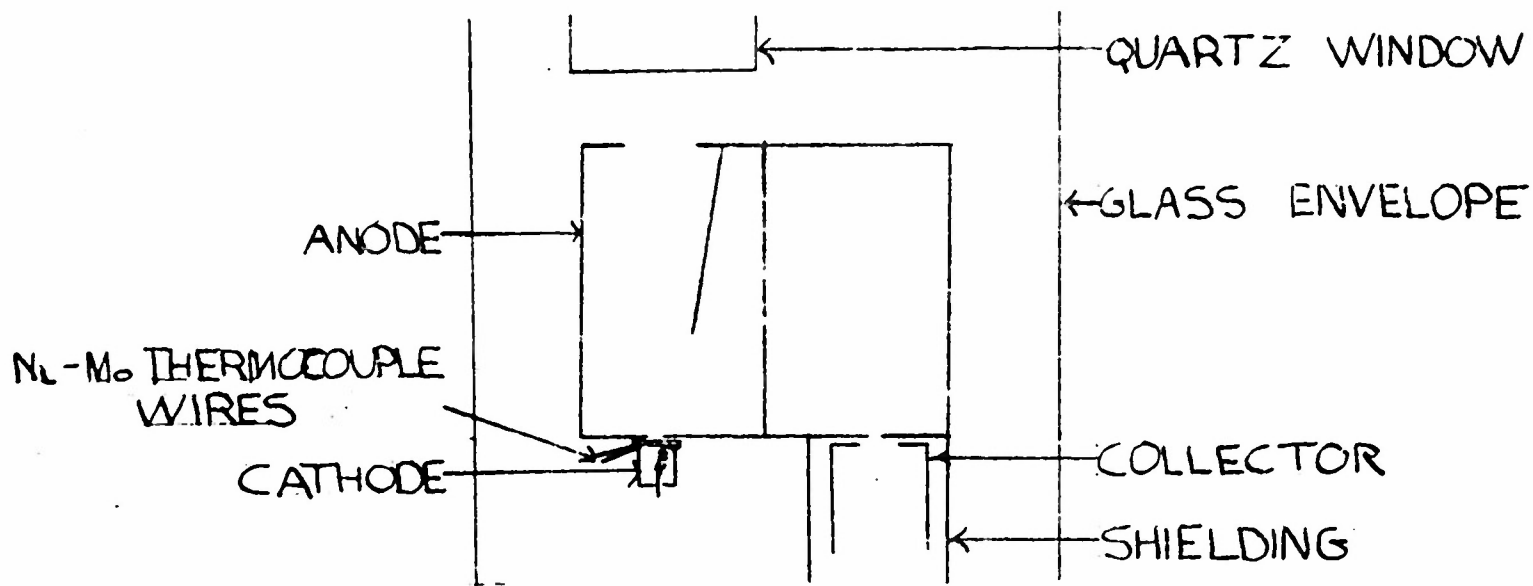
Mr. Spicer who has been doing this field emission work is not engaged in research this semester. The field emission problem is not being followed further at this time. Work on it may be resumed at some later time.

9. Enhanced Photoelectric Effect in BaO - (Philipp)

A tube containing a magnetic velocity analyser was built for obtaining the energy distribution of photoelectrons. The analyser sketched below was constructed entirely of tantalum and has a three centimeter diameter semicircular deflecting path. This path is defined by three slits, two 1/2 mm slits and one 1 1/2 mm slit located just above the cathode position. A pair of 29 inch diameter Helmholtz coils were built to give a uniform magnetic field.

A tungsten filament was mounted in the cathode position to serve as a source of electrons for studying the characteristics of the analyser and for calibration of the analyser and Helmholtz coils. A compressed air driven, magnetic null indicator was constructed to determine when the vertical

component of the earth's field had been cancelled. The small horizontal component does not affect the trajectories in the plane of the diagram.



A Gaertner thermopile has been used in previous photoelectric measurements to monitor the intensity of the irradiating light. Some consideration has been given to using in its place a type 935 phototube with a Cs Sb surface which acts as a black body receiver in the far ultraviolet. A 935 tube was calibrated, using Mr. Gandy's apparatus, against a thermister bolometer. The spectral response curve obtained appears good from 700 to 280 $m\mu$ but below this it is believed that the results are influenced by scattered light from the visible region. This calibration will be repeated

using filters to minimize the effect of scattered light.

10 a. Photoelectric Emission from Impurity Centers - (Goodman)

The broad energy distribution of photoelectrons from trapping centers is attributed to the displacement of the electronic states by the motion of the atoms around the trap. The formal expression for the kinetic energy distribution was given in the last Progress Report. The energy spread was represented by a function $H(h(\nu - \nu_f))$ which gives the relative probability that the lattice will absorb the energy difference $h(\nu - \nu_f)$ in excess of the amount corresponding to a transition "vertically upward" in the Franck-Condon sense.

For F-centers this broadening should be very similar in shape to the F-absorption band. It was intended to calculate H for a material like RbI by a direct extension to the bound-free transition of the theory of F-center absorption developed independently by Huang and Rhys¹⁰ and by Pekar¹¹. In the latter work especially there are a number of numerical results in the shape of the F-band which seem to be in good agreement with what is observed. However, in both papers agreement can be obtained only by using a dielectric continuum model for the crystal which has no hole for the missing

10. K. Huang and A. Rhys, Proc. Roy. Soc. A 204, 406 (1950).

11. C.I. Pekar, J.E. T.P. 20, 510 (1950).

halogen ion. Only for this case is the interaction between the polarization of the lattice and the charge distribution of the trapped electron large enough to give the observed width of the F-band. This model should be good when the orbit size of the electronic states is large compared with the radius of the vacancy.

The wave functions used by Pekar¹² for the value of the parameter which gives the good "fit" have an orbit radius about equal to a_0 which is much smaller than the radius of the vacancy and therefore is meaningless. The F-center wave functions obtained by Simpson¹³ with a more realistic model of the center are confined largely to the interior of the hole left by the missing ion. Huang and Rhys have calculated that these states have too weak an electrostatic interaction with the lattice.

It seems that the trapped electron is localized in the atoms just around the vacancy and that the interaction involves changes in kinetic energy, etc., in addition to the electrostatic effects considered previously. This picture is in accord with the recent result of Kahn and Kittel¹⁴ that the ground state of the F-center has large non spherically symmetric components correspond-

12. C.I. Pekar and M.F. Dyeigen, J.E.T.P. 18, 481 (1948).

13. J.H. Simpson, Proc. Roy. Soc. A 197, 269 (1949).

14. A.H. Kahn and C. Kittel, Phys. Rev. 89, 315 (1952).

ing to the motion of the electron around the six nearest neighbor alkali ions. A calculation of the energy broadening to be expected on this basis has not yet been made.

10 b. Long Life Luminescence and Diffusion by Retrapping

The possibility is being considered that the time dependence of the long life luminescence in MgO observed by Eisenstein is determined by a diffusion process. This is suggested by some properties of the luminescence.

a) The low increase power ($\sim \frac{1}{2}$ at room temperature) low time decay. $t^{-\frac{1}{2}}$ is a characteristic time dependence in simple diffusion problems.

b) The decay law depends on the amount of irradiation. This is hard to understand on the basis of a distribution of depth of the traps from which the electron (or holes) must be released before they can recombine with the luminescence centers. On the other hand the spatial distribution of released electrons will change with the length of the irradiation.

Debye and Edwards¹⁵ have studied the fairly long time decay of UV excited luminescence of organic phosphors imbedded in rigid glasslike media. Here too the luminescence decay follows an inverse power law and a range of values of the exponent is observed. They have shown that it is possible to understand theoretically a power recombination rate for the electrons released by the UV from the luminescence centers. In particular, they

15. P. Debye and J.O. Edwards, J. Chem. Phys. 20, 236 (1952).

showed that a definite probability distribution of the distance that the released electron travels from its center before the UV is turned off will give a power law recombination rate if the subsequent behavior of the distribution is governed by the diffusion equation. They do not show that this distribution will result from the original release process. However, the shape of the necessary distribution with its maximum at some distance from the luminescence center is physically reasonable.

Almost any other decay law can be explained by some corresponding distribution because the solution of the diffusion equation involves a sum (or integral) of terms with an $e^{-\epsilon t}$ time dependence and the representation of a predetermined function of time by such a sum is just a Laplace transformation.

The following two problems have been considered:

1) Determination of initial distribution

This model is probably more applicable to UV excitation than x-ray excitation. All the electrons are assumed to come originally by release from luminescence centers at a rate proportional to the number not yet released (constant irradiation intensity). There is one electron at each center originally. Recombination takes place during the irradiation.

The formal solution of the problem has been obtained but no analytical approximations have been found yet and further work may have to be

numerical. This is unpleasant because the parameters involved are not known.

2) Luminescence from a uniform distribution.

It is likely that x-rays release many electrons in addition to those originally in the luminescence centers. When the x-rays are turned off and after electron-hole recombination the resulting electron distribution should be more nearly uniform than in the first model. The recombination rate has been calculated for an initially uniform distribution and regularly spaced absorbing luminescent centers. A Wigner-Seitz approximation was made in which each center is surrounded by an equivalent sphere and the boundary condition $\frac{\partial m(r,t)}{\partial r} = 0$ is applied at the radius of the spheres. The recombination rate is:

$$\text{Eq. 1} \quad K(t) = 8\pi D m_0 a \sum_{p=1}^{\infty} e^{-\lambda_p^2 \frac{Dt}{a^2}} \cdot \frac{\left(1 + \frac{\epsilon^2}{\lambda_p^2}\right)}{\left(1 - \frac{\epsilon^3}{\lambda_p^2(1-\epsilon)}\right)} ;$$

m_0 is the initial density of electrons

D is the diffusion coefficient

a is the "radius" of the absorbing center

R is the radius of the equivalent sphere

$\epsilon = \frac{a}{R}$ is probably a small number

λ_p is the p^{th} root excluding $\lambda = 0$ of $\cot \left\{ \frac{(1-\epsilon)}{\epsilon} \lambda \right\} = \frac{\epsilon}{\lambda}$.